FOUNDATIONS OF QUANTUM DYNAMICS

S. M. BLINDER

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PREFACE

The subject of this monograph is the mathematical formalism of nonrelativistic quantum dynamics. The structure and foundations of this formalism are examined in detail with emphasis on fundamental principles rather than concrete applications. Still, our approach is slanted towards application to the domains of molecular physics and quantum chemistry. Our scope is thus limited to nonrelativistic wave mechanics and semiclassical radiation theory. We stop short of more advanced developments including the Dirac equation, quantum electrodynamics, formal scattering theory, density matrices and diagram techniques. These latter topics are, in fact, quite adequately covered in a number of current textbooks. I might suggest, however, that this monograph will prove of some value in bridging the gap between elementary wave mechanics and these more advanced techniques.

We begin, in Chapter 1, with a brief survey of some relevant topics in classical mechanics: Hamiltonian dynamics, Poisson brackets and Hamilton–Jacobi theory. Chapter 2 covers classical electrodynamics on the level of the Maxwell–Lorentz equations, emphasizing those aspects which pertain to radiative transitions in atoms and molecules. Special relativity is also developed as an outgrowth of electrodynamics. In subsequent chapters, points of connection between quantum-dynamical formalism and these classical theories are analyzed in detail. Chapter 3 reviews the postulates and general principles of quantum mechanics, including a few fine points which are usually glossed over in both elementary and advanced treatments. Chapter 4 is about time-dependent quantum mechanics, mainly the time-dependent Schrödinger equation. In chapter 5, the formalism of quantum dynamics is applied to the free particle. Some discussion is also given on continuum eigenstates and on the basic ideas of potential scattering. Chapter 6 is about Green's functions, both as mathematical tools used elsewhere and, in their own right, as the basis of high-powered computational formalism. Chapter 7 concerns transitions among quantum states and their treatment by time-dependent perturbation theory. In the final chapter we consider first the semiclassical theory of electromagnetic interactions. Our line of development then culminates in a fairly extensive discussion of radiative

transitions in atomic and molecular systems. Two appendices give some required material on the Dirac deltafunction and Fourier analysis.

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S.M.B.
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1

Classical Dynamics*

In this chapter we shall briefly survey those parts of classical dynamics which have particular relevance to quantum theory. Principal among these are Hamiltonian formalism, equations of motion in Poisson bracket form and Hamilton–Jacobi theory.

1.1 Lagrange's Equations

It is assumed that the reader is familiar with the derivation of Lagrange's equations starting with Newton's equations of motion. We shall outline here an alternative derivation based on Hamilton's principle.

Let the dynamical structure of a classical system be characterized by some function $L(q, \dot{q}, t)$ of the n generalized coordinates q_i, n generalized velocities $\dot{q}_i$ $(i = 1 \ldots n)$ and time t. The kinematical behaviour of the system is described by a *trajectory*, i.e. a set of functional relations

$$q_i = q_i(t), \qquad i = 1 \ldots n \tag{1.1.1}$$

consistent with the constraints imposed on the system. The task is now to relate kinematics with dynamics. Assume that one can parametrically represent every conceivable trajectory connecting configuration $q_1^{(0)} \ldots q_n^{(0)}$ at an initial time t_0 with configuration $q_1^{(1)} \ldots q_n^{(1)}$ at a later time t_1. One of these paths will represent the *actual* motion of the system between times t_0 and t_1. *Hamilton's principle* is the postulate that the time integral of $L(q, \dot{q}, t)$ assumes a stationary value along the actual trajectory, i.e.,

$$\delta \int_{t_0}^{t_1} L(q, \dot{q}, t)\, \mathrm{d}t = 0, \tag{1.1.2}$$

in which δ represents variation of the parameters determining a trajectory. In terms of differential variations in the q_i and $\dot{q}_i$ at each point in time, one can also write

$$\int_{t_0}^{t_1} \sum_{i=1}^{n} \left(\frac{\partial L}{\partial q_i} \delta q_i + \frac{\partial L}{\partial \dot{q}_i} \delta \dot{q}_i \right) \mathrm{d}t = 0. \tag{1.1.3}$$

* For a more complete treatment of the subject, there is no finer reference than H. Goldstein, *Classical Mechanics* (Addison-Wesley, Cambridge, Massachusetts, 1951).

Noting that

$$\delta\dot{q}_i = \frac{\mathrm{d}}{\mathrm{d}t}\delta q_i \tag{1.1.4}$$

the second summation can be integrated by parts:

$$\int_{t_0}^{t_1} \frac{\partial L}{\partial \dot{q}_i}\frac{\mathrm{d}}{\mathrm{d}t}(\delta q_i)\,\mathrm{d}t = \frac{\partial L}{\partial \dot{q}_i}\delta q_i\Big]_{t_0}^{t_1} - \int_{t_0}^{t_1}\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial L}{\partial \dot{q}_i}\right)\delta q_i\,\mathrm{d}t. \tag{1.1.5}$$

The boundary terms vanish since, by supposition, the initial and final configurations of the system are specified, i.e.

$$\delta q_i^{(0)} = 0, \quad \delta q_i^{(1)} = 0. \tag{1.1.6}$$

Hamilton's principle thereby reduces to

$$\int_{t_0}^{t_1}\sum_{i=1}^{n}\left\{\frac{\partial L}{\partial q_i} - \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial L}{\partial \dot{q}_i}\right)\right\}\delta q_i\,\mathrm{d}t = 0. \tag{1.1.7}$$

Now if the δq_i can be arbitrarily varied *independently of one another* (holonomic system), each curly bracket must individually vanish. We arrive thus at *Lagrange's equations of motion*

$$\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial L}{\partial \dot{q}_i} - \frac{\partial L}{\partial q_i} = 0, \quad i = 1 \ldots n. \tag{1.1.8}$$

Solution of these equations, consistent with a set of specified initial conditions, say, $q_i^{(0)}$ and $\dot{q}_i^{(0)}$ $(i = 1 \ldots n)$, suffices in principle to determine each generalized coordinate as a function of time (eqn 1.1.1).

We have yet however to specify the functional form of the *Lagrangian* $L(q, \dot{q}, t)$. It is suggestive to consider the motion of a particle in a conservative field of force. By Newton's second law,

$$m\ddot{\mathbf{r}} = -\nabla V(\mathbf{r}), \tag{1.1.9}$$

noting that conservative forces can be represented as the negative gradient of a potential energy. In cartesian coordinates, the equations of motion take the form

$$m\ddot{x}_i + \frac{\partial V}{\partial x_i} = 0, \qquad i = 1, 2, 3. \tag{1.1.10}$$

It is easily seen that these are isomorphous with (1.1.8) provided that one identifies

$$L(\mathbf{r}, \dot{\mathbf{r}}) = \tfrac{1}{2}m\dot{\mathbf{r}}^2 - V(\mathbf{r}). \tag{1.1.11}$$

In the great majority of cases, the Lagrangian is simply the difference between the kinetic and potential energies

$$L = T - V. \tag{1.1.12}$$

Should there arise some ambiguity in defining T or V, however, one has recourse to the fundamental significance of the Lagrangian as that function which establishes (1.1.8) as the equations of motion governing the system.

Consider, for example, the equation for a damped harmonic oscillator:

$$m\ddot{x} + \eta\dot{x} + kx = 0. \tag{1.1.13}$$

Because of the velocity-dependent dissipative force $-\eta\dot{x}$, the Lagrangian *cannot* be represented in the form (1.1.12). It is easily verified however that (1.1.13) can be derived from a time-dependent Lagrangian†

$$L(x, \dot{x}, t) = e^{\gamma t}(\tfrac{1}{2}m\dot{x}^2 - \tfrac{1}{2}kx^2), \qquad \gamma \equiv \eta/m. \tag{1.1.14}$$

1.2 Hamiltonian Dynamics

For conservative systems, in which the Lagrangian contains no explicit time dependence, i.e.

$$\partial L/\partial t = 0, \tag{1.2.1}$$

an important conservation principle applies. To demonstrate this, multiply each Lagrange equation (1.1.8) by the corresponding $\dot{q}_i$ and sum:

$$\sum_i \left(\dot{q}_i \frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial L}{\partial \dot{q}_i} - \dot{q}_i \frac{\partial L}{\partial q_i} \right) = 0. \tag{1.2.2}$$

Note now that

$$\frac{\mathrm{d}L}{\mathrm{d}t} = \sum_i \left(\frac{\partial L}{\partial q_i}\dot{q}_i + \frac{\partial L}{\partial \dot{q}_i}\ddot{q}_i \right) \tag{1.2.3}$$

and

$$\frac{\mathrm{d}}{\mathrm{d}t}\sum_i \frac{\partial L}{\partial \dot{q}_i}\dot{q}_i = \sum_i \left(\dot{q}_i \frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial L}{\partial \dot{q}_i} + \frac{\partial L}{\partial \dot{q}_i}\ddot{q}_i \right). \tag{1.2.4}$$

Subtracting (1.2.3) from (1.2.4) and substituting into (1.2.2), we find

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\sum_i \frac{\partial L}{\partial \dot{q}_i}\dot{q}_i - L \right) = 0. \tag{1.2.5}$$

† For systems subject to forces which are not entirely conservative, Lagrange's equations can be generalized to

$$\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial L}{\partial \dot{q}_i} - \frac{\partial L}{\partial q_i} = Q_i, \qquad i = 1 \ldots n \tag{1.1.8'}$$

which Q_i is the dissipative force associated with the ith degree of freedom. Thus, (1.1.13) can alternatively be represented using

$$L = \tfrac{1}{2}m\dot{x}^2 - \tfrac{1}{2}kx^2, \qquad Q = -\eta\dot{x}. \tag{1.1.14'}$$

Thus the *Hamiltonian function*

$$H \equiv \sum_i \frac{\partial L}{\partial \dot{q}_i} \dot{q}_i - L \tag{1.2.6}$$

is constant in time for a conservative system.

When L contains explicit time dependence, then H will as well. Equation (1.2.6) represents, in fact, a *Legendre transformation* in which the $\dot{q}_i$ are displaced as fundamental variables by the quantities $\partial L/\partial \dot{q}_i$. This is made explicit by taking the total differential of (1.2.6), noting that L is a function of the q_i, $\dot{q}_i$ and t:

$$\mathrm{d}H = \sum_i \left\{ \dot{q}_i \, \mathrm{d}\left(\frac{\partial L}{\partial \dot{q}_i}\right) + \frac{\partial L}{\partial \dot{q}_i} \mathrm{d}\dot{q}_i \right\} - \sum_l \left\{ \frac{\partial L}{\partial q_i} \mathrm{d}q_i + \frac{\partial L}{\partial \dot{q}_i} \mathrm{d}\dot{q}_i \right\} - \frac{\partial L}{\partial t} \mathrm{d}t. \tag{1.2.7}$$

The terms in $\mathrm{d}\dot{q}_i$ cancel, thus indicating that the new function H depends on the variables q_i, $\partial E/\partial \dot{q}_i$ and t.

The new variables

$$p_i \equiv \partial L/\partial \dot{q}_i \tag{1.2.8}$$

are known as *generalized momenta.* In cartesian coordinates, (1.2.8) reduces to the usual definition of linear momentum. For example, with (1.1.11),

$$p_x = \frac{\partial L}{\partial \dot{x}} = m\dot{x} \tag{1.2.9}$$

The corresponding pairs of generalized coordinates and momenta q_i, p_i are known as *conjugate variables.* Their product invariably has dimension ml^2/t, known as *action.* Thus, length and linear momentum, angle and angular momentum, time and energy are the common pairs of conjugate variables. In quantum theory, the fundamental constant $\hbar$ has dimensions of action while each pair of conjugate variables is governed by an uncertainty relation (cf Section 3.6A).

One can now write

$$H(q, p, t) \equiv \sum_i p_i \dot{q}_i - L(q, \dot{q}, t) \tag{1.2.10}$$

and, using (1.2.8) in (1.2.7),

$$\mathrm{d}H = \sum_i (\dot{q}_i \, \mathrm{d}p_i - \dot{p}_i \, \mathrm{d}q_i) - \frac{\partial L}{\partial t} \mathrm{d}t. \tag{1.2.11}$$

Evidently,

$$\partial H/\partial p_i = \dot{q}_i, \quad \partial H/\partial q_i = -\dot{p}_i, \qquad i = 1 \ldots n \tag{1.2.12}$$

and

$$\partial H/\partial t = -\partial L/\partial t. \tag{1.2.13}$$

Equations (1.2.12) are *Hamilton's equations of motion.* Usually the second of these is equivalent Newton's second law in the form

$$\dot{p}_i = F_i \tag{1.2.14}$$

while the first relates p_i to the generalized velocity. Equations (1.2.12) are also known, because of their theoretical importance, as *canonical equations of motion.* The q_i, p_i entering into these equations are correspondingly denoted *canonical variables.*

Comparison of (1.1.8) with (1.2.13) shows that a mechanical problem can be formulated either as a set of n second-order differential equations (Lagrange's) or as a set of $2n$ first-order differential equations (Hamilton's). In either case, $2n$ initial or boundary conditions are required for a complete solution.

Except under some rather exotic circumstances, the Hamiltonian function represents the total energy of a system†. Consider a Lagrangian in the form

$$L = T - V_0 - V_1. \tag{1.2.15}$$

in which the kinetic energy is a homogeneous quadratic function of the generalized velocities which does *not* involve the time explicitly, i.e.

$$T = \tfrac{1}{2} \sum_{i,j} a_{ij}(q)\dot{q}_i\dot{q}_j \tag{1.2.16}$$

while the potential energy, which may depend on t, contains (at most) a homogeneous linear dependence on generalized velocities, i.e.

$$V_0 = V_0(q, t), \qquad V_1 = \sum_i b_i(q, t)\dot{q}_i. \tag{1.2.17}$$

By Euler's theorem on homogeneous functions, we have

$$\sum_i \frac{\partial T}{\partial \dot{q}_i}\dot{q}_i = 2T \quad \text{and} \quad \sum_i \frac{\partial V}{\partial \dot{q}_i}\dot{q}_i = V. \tag{1.2.18}$$

† For the damped harmonic motion represented by the Lagrangian (1.1.14), the general prescription for constructing the Hamiltonian gives

$$p = \frac{\partial L}{\partial \dot{x}} = e^{\gamma t} m\dot{x} \tag{1.2.21}$$

and thus

$$H(x, p, t) = e^{-\gamma t}\frac{p^2}{2m} + e^{\gamma t}\frac{kx^2}{2}. \tag{1.2.22}$$

The sum of the kinetic and potential energies is however

$$E = \tfrac{1}{2}m\dot{x}^2 + \tfrac{1}{2}kx^2 \tag{1.2.23}$$

so that $H = e^{\gamma t}E$—one of those pathological instances in which $H \neq E$. If, however, one defines the Lagrangian in accordance with (1.1.8′) and (1.1.14′), a Hamiltonian equal to (1.2.23) is obtained.

Putting (1.2.15) into (1.2.6) and making use of (1.2.18), we find that

$$H = T + V_0 \equiv E \tag{1.2.19}$$

(V_1 having cancelled out). Under the very general circumstances considered, the Hamiltonian represents the sum of the ordinary kinetic and potential energies, hence the total energy of the system. When V_0 is time dependent, then E, as defined, will also be time dependent. When V_0 is independent of time, then, in accordance with (1.2.5), the energy of the system is conserved.

For a particle in a conservative field, application of (1.2.9) and (1.2.10) to the Lagrangian (1.1.11) leads to the Hamiltonian function

$$H(\mathbf{r}, \mathbf{p}) = \frac{p^2}{2m} + V(\mathbf{r}) \tag{1.2.20}$$

This is representative of a large number of instances in which the Hamiltonian can be constructed simply by expressing the energy as a function of generalized coordinates and momenta.

The Hamiltonian formulation of mechanics outlined in this section is entirely equivalent in physical content to the Lagrangian formulation. In fact, Hamilton's equations (1.2.13) often reduce to the very same differential equations as Lagrange's equations (1.1.8). Hamiltonian dynamics nonetheless possess a number of conceptual advantages. One is the physical significance of the Hamiltonian function itself. A second attractive feature is the near symmetry in the roles of generalized coordinates and momenta. These can accordingly be employed with greater flexibility than the variables in Lagrangian formalism. In consequence, Hamiltonian dynamics plays an important role in the formulation of both quantum theory and statistical mechanics.

1.3 Equations of Motion for Dynamical Variables

Let $A(q, p, t)$ represent some physical property of the dynamical system expressed as a function of canonical variables and time. As the system evolves in conformity with Hamilton's equations, each dynamical variable A will correspondingly vary with time in accordance with

$$\frac{\mathrm{d}A}{\mathrm{d}t} = \frac{\partial A}{\partial t} + \sum_{i=1}^{n} \left(\frac{\partial A}{\partial q_i} \dot{q}_i + \frac{\partial A}{\partial p_i} \dot{p}_i \right). \tag{1.3.1}$$

By substituting for $\dot{q}_i$ and $\dot{p}_i$ from (1.2.13) we obtain

$$\frac{\mathrm{d}A}{\mathrm{d}t} = \frac{\partial A}{\partial t} + \sum_{i=1}^{n} \left(\frac{\partial A}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial A}{\partial p_i} \frac{\partial H}{\partial q_i} \right). \tag{1.3.2}$$

It is useful to define the *Poisson bracket* of two dynamical variables A and

B as follows:

$$\{A, B\} \equiv \sum_{i=1}^{n} \left(\frac{\partial A}{\partial q_i} \frac{\partial B}{\partial p_i} - \frac{\partial B}{\partial q_i} \frac{\partial A}{\partial p_i} \right). \tag{1.3.3}$$

It can be shown that this quantity is invariant to alternative choices of the canonical variables in a given system. Since Poisson brackets provide an important link to quantum mechanics, we shall summarize some of their properties. The following identities are readily demonstrated:

$$\{A, A\} = 0 \tag{1.3.4}$$

$$\{A, B\} = -\{B, A\} \tag{1.3.5}$$

$$\{A, B + C\} = \{A, B\} + \{A, C\} \tag{1.3.6}$$

$$\{A^2, B\} = 2A\{A, B\} \tag{1.3.7}$$

$$\{A, BC\} = C\{A, B\} + B\{A, C\} \tag{1.3.8}$$

and

$$\{\{A, B\}, C\} + \{\{B, C\}, A\} + \{\{C, A\}, B\} = 0. \tag{1.3.9}$$

(Jacobi's identity)

When A and B are canonical variables themselves, we find

$$\{q_i, q_j\} = 0, \quad \{p_i, p_j\} = 0 \quad \text{all } i, j \tag{1.3.10}$$

but

$$\{q_i, p_j\} = \delta_{ij}. \tag{1.3.11}$$

Returning now to the equation of motion (1.3.2), we recognize that it can be written

$$\frac{\mathrm{d}A}{\mathrm{d}t} = \frac{\partial A}{\partial t} + \{A, H\}. \tag{1.3.12}$$

This points up that, besides its significance as the energy, the Hamiltonian also governs the time development of all dynamical variables. When applied to the canonical variables, (1.3.12) reproduces Hamilton's equations in Poisson bracket form:

$$\dot{q}_i = \{q_i, H\} \tag{1.3.13}$$

and

$$\dot{p}_i = \{p_i, H\}. \tag{1.3.14}$$

When A is the Hamiltonian itself, then, because of (1.3.4),

$$\frac{\mathrm{d}H}{\mathrm{d}t} = \frac{\partial H}{\partial t}. \tag{1.3.15}$$

Thus $H(q, p)$ with no *explicit* dependence on time will maintain a constant value even as the coordinates and momenta vary with time in the course of the system's motion. This is consistent, of course, with the conservation of energy in a conservative system.

A dynamical variable for which $\mathrm{d}A/dt = 0$ is known as a *constant of the motion*. According to (1.3.12), a constant of the motion must fulfil two conditions:

$$\partial A/\partial t = 0 \quad \text{and} \quad \{A, H\} = 0. \tag{1.3.16}$$

1.4 Hamilton–Jacobi Theory

We shall present an *ad rem* derivation of the Hamilton–Jacobi equation which does not explicitly develop its connection with either canonical transformations or variational principles. *Hamilton's principal function* (sometimes called, rather loosely, the *action integral*) is defined as

$$S(q, q^{(0)}, t) \equiv \int_0^t L(q', \dot{q}', t')\,\mathrm{d}t'. \tag{1.4.1}$$

It is presumed that the integrand describes an *actual* trajectory of the system during the time interval 0 to t, such that $\delta S = 0$, in accord with Hamilton's principle. The trajectory is characterized by the set of functional relations

$$q_i' = q_i'(t'), \quad \dot{q}_i' = \dot{q}_i'(t'), \quad i = 1 \ldots n, \tag{1.4.2}$$

obtained by solution of the equations of motion subject to the initial and final conditions

$$q_i'^{(0)} = q_i^{(0)}, \; q_i'(t) = q_i, \quad i = 1 \ldots n. \tag{1.4.3}$$

Incorporating (1.4.3) very explicitly into (1.4.2), we can write

$$q_i' = q_i'(q, q^{(0)}, t, t'), \quad \dot{q}_i' = \dot{q}_i'(q, q^{(0)}, t, t'), \quad i = 1 \ldots n \tag{1.4.4}$$

and correspondingly,

$$S(q, q^{(0)}, t) = \int_0^t L[q'(q, q^{(0)}, t, t'), \; \dot{q}'(q, q^{(0)}, t, t'), t']\,\mathrm{d}t'. \tag{1.4.5}$$

Now

$$\frac{\partial S}{\partial q_i} = \int_0^t \sum_{j=1}^{n} \left(\frac{\partial L}{\partial q_j'} \frac{\partial q_j'}{\partial q_i} + \frac{\partial L}{\partial \dot{q}_j'} \frac{\partial \dot{q}_j'}{\partial q_i} \right) \mathrm{d}t'. \tag{1.4.6}$$

Noting that

$$\left.\begin{aligned} \frac{\partial L}{\partial \dot{q}_j'} &= p_j' \\ \text{and} \qquad & \\ \frac{\partial L}{\partial \dot{q}_j'} &= \frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial L}{\partial \dot{q}_j'} = \dot{p}_j' \end{aligned}\right\} \tag{1.4.7}$$

we can write

$$\frac{\partial S}{\partial q_i} = \int_0^t \frac{\mathrm{d}}{\mathrm{d}t}\left(\sum_j p_j' \frac{\partial q_j'}{\partial q_i}\right)\mathrm{d}t'$$

$$= \sum_j p_j' \frac{\partial q_j'}{\partial q_i}\Bigg]_0^t = \sum_j \left(p_j \frac{\partial q_j}{\partial q_i} - p_j^{(0)} \frac{\partial q_j^{(0)}}{\partial q_i}\right). \tag{1.4.8}$$

Thus

$$\partial S/\partial q_i = p_i, \quad i = 1 \ldots n. \tag{1.4.9}$$

Analogously, it is shown that

$$\partial S/\partial q_i^{(0)} = -p_i^{(0)}, \quad i = 1 \ldots n \tag{1.4.10}$$

Consider now the time derivative of S:

$$\frac{\partial S}{\partial t} = L(q, \dot{q}, t) + \int_0^t \sum_i \left(\frac{\partial L}{\partial q_i'}\frac{\partial q_i'}{\partial t} + \frac{\partial L}{\partial \dot{q}_i'}\frac{\partial \dot{q}_i'}{\partial t}\right)\mathrm{d}t'. \tag{1.4.11}$$

The last integral can analogously be transformed to

$$\sum_i p_i' \frac{\partial q_i'}{\partial t}\Bigg]_0^t \tag{1.4.12}$$

Applying the identity

$$\left(\frac{\partial q_i'}{\partial t}\right)_{q_i} = -\left(\frac{\partial q_i}{\partial t}\right)_{q_i'}\left(\frac{\partial q_i'}{\partial q_i}\right)_t \tag{1.4.13}$$

this becomes

$$-\sum_i \left(p_i \dot{q}_i - p_i^{(0)} \dot{q}_i^{(0)} \frac{\partial q_i^{(0)}}{\partial q_i}\right) \tag{1.4.14}$$

Thus

$$\frac{\partial S}{\partial t} = L - \sum_i p_i \dot{q}_i = -H. \tag{1.4.15}$$